Linking Monte Carlo Simulation and Target Transformation Factor Analysis: A Novel Tool for EXAFS Analysis

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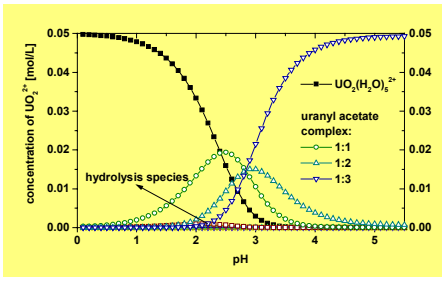
INTRODUCTION

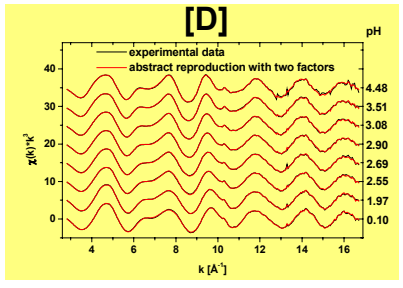
- Uranyl speciation in aqueous solutions is often complex, since several species may coexist at one pH
- Advanced statistical methods like Target Transformation Factor Analysis (TFA) or Iterative TFA /1/, which are able to extract single species from the EXAFS spectra of mixtures, require as input information either
  - ⇒ the XAFS spectra of the pure species
  - ⇒ ***or*** the concentration of the species in the mixture /2,3/.
- However, often such spectra do not exist, since the species cannot be prepared in pure form, ***and*** the species concentration is unknown.
- We have developed a new method, to determine the structure in solution. The new method **MCTFA** links Monte-Carlo simulation (MC) to TFA.
- To test our approach, we have used a system with known pH-speciation (0.05 M U(VI), 1.0 M acetic acid in the pH range 0.1 to 4.5).

Analysis of Model System /2/

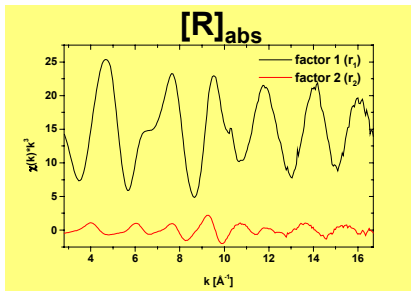
Calculated pH speciation
RAMESES, I = 1.3 mol/L, 1.0 mol/L acetic acid /4/



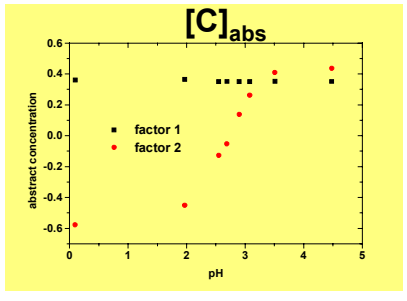
$U\text{-}L_{III}$ EXAFS spectra (black) and their abstract reproductions (Eigenanalysis, red)



Abstract EXAFS spectra (Eigenvectors)

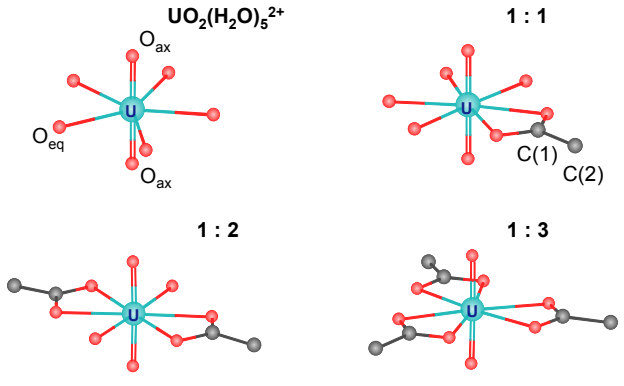


Abstract concentrations (Eigenvectors)



➢The data are reproduced by **[D] = $[R]_{abs}$* $[C]_{abs}$**.

➢Only two spectroscopic components are required to describe the variation of spectra: U-H_2O and U-carboxylate



EXAFS fit of the two spectral components

	Atom	R [Å]	N	σ^2*10^{-3} [Å]^2
U-H_2O	O_{ax}	1.77	2.0	1.3
	O_{eq}	2.41	5.3	7.2
U-carboxylate	O_{ax}	1.78	2.0	1.4
	O_{eq}	2.47	6.0	8.5
	C(1)	2.87	3.1	3.8
	C(2)	4.39	3.1	3.8

Conclusions

- From the EXAFS spectra of mixtures of aqueous uranyl and several U-acetate complexes, we could derive the structure of the U-carboxylate unit.
- Neither the spectra of the pure species nor their concentrations were required.
- The newly developed **MCTFA** approach should be suited to solve the structure of much larger complexes, e.g. involving lignin or even NOM.
- However, the computing time will drastically increase. Our relatively simple calculations took 110,000 steps and 10 min on a PIII 1.2 GHz to converge.

Application of MCTFA

Objective:

Determination of the structure of U(VI)/acetic acid complexes under ill-defined conditions (mixture of species, short k-range: 3-12 Å^{-1}, small number of spectra: 4, pH 0.10 – 2.69)

MCTFA Procedure

- Fit of spectrum pH 2.69 to determine Debye-Waller factor σ_{eq} for O_{eq} and energy shift ΔE using FEFF and uranyl triacetate /5/ (Table 2).
- Calculate $[R]_{abs}$ and Eigenvalues $[\Lambda]$ using the spectra pH 0.10 – 2.69
- Set up a cube with edge length 6 Å, insert acetate molecule such that C(1) is in the center of the cube, put U-atom at a random position in the cube. Calculate distances R_i between U and acetate atoms.
- Calculate the theoretical EXAFS spectrum (vector x_{test}) using R_i and the fit values of O_{ax}, σ^2_{eq}, ΔE (Table bottom, σ^2 of C(1) and C(2) was set to 0.004 Å^2).
- Introduce x_{test} as target test vector into the TFA procedure; this yields the predicted vector $x_{pred} = [R]_{abs} * [\Lambda]^{-1} * [R]' * x_{test}$.
- Determine chi^2 between x_{pred} and x_{test} and normalize to variance (x_{pred}^2), save the best normalized chi^2.
- Go to step (3) and repeat 5000 times.
- Put U-atom at the position of the lowest normalized chi^2, divide edge length of cube by 1.3. If edge length > 0.02 Å then go to step (3)
- U-atom has reached the optimum position towards the ligand

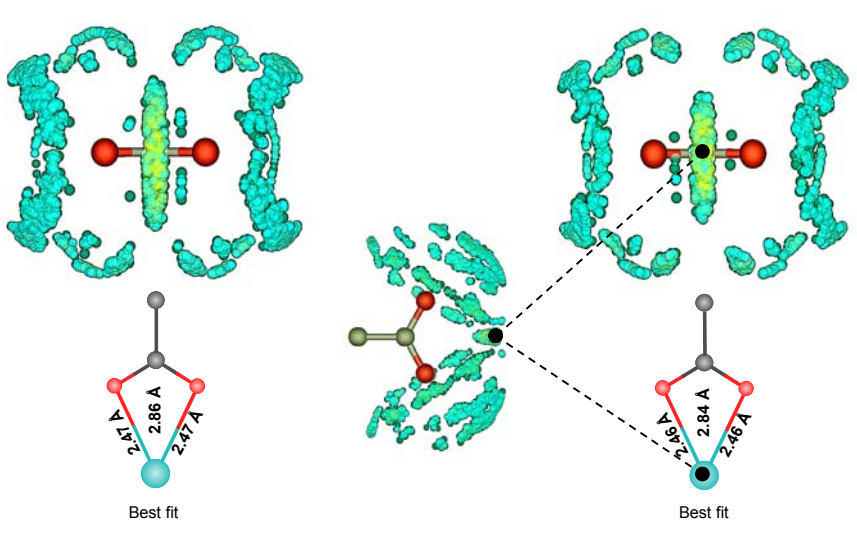
MCTFA Results

U density distributions around the acetate molecule

(yellow balls indicate best fits, blue balls bad fits)

MC simulation using experimental EXAFS spectrum of the pure species (pH 4.48)

MCTFA using „ill-defined“ spectra (pH 0.1 – 2.69)



Best fit

Best fit

MCTFA results (red: fitted, green: fixed)

Atom	R [Å]	N	σ^2*10^{-3} [Å]^2
O_{ax}	1.78	2	1.7
O_{eq}	**2.46**	4	9.5
C(1)	**2.84**	2	4
C(2)	**4.34**	2	4

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